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MEMORANDUM

SUBJECT: Telephone Conversation with Chrysler

FROM: John A. Garbak, Environmental Engineer
Fuels Section

THROUGH: James W. Caldwell, Chief
Fuels Section

Steven E. Hoover, Acting Branch Chief
Field Operations and Compliance Policy Branch

Mary T. Smith, Director
Field Operations and Support Division

TO: Docket No. A-90-16

On August 3, 1990 I had a telephone conversation with Mike Brady and Frank Krich of Chrysler Corporation. The call was to obtain further information from Chrysler regarding their theory as to why the catalysts efficiencies were better for vehicles operated with MMT than for the vehicles operated without the MMT.

Chrysler stated that without the MMT in the fuel any poisons in the fuel such as lead or phosphorus will block sites in the catalyst and make the catalyst less active. With the MMT in the fuel Mn oxide acts as a scavenger and picks up the poisons such as lead and phosphorus. (SAE paper 821193 discusses this and is attached.) This activity will make the catalyst more efficient since the lead and phosphorus won't block the sites. The phosphorus comes from the oil and lead, even at the low levels in unleaded, has some effect.

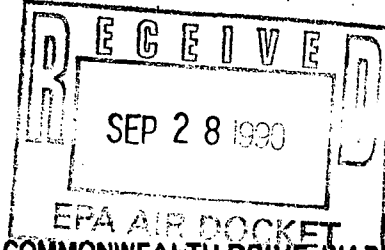
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Effects of Fuel Additive MMT on Contaminant Retention and Catalyst Performance

W. B. Williamson and H. S. Gandhi

Engineering and Research Staff
Ford Motor Co.

E. E. Weaver

Automotive Emissions and Fuel Economy Office
Ford Motor Co.

Fuels and Lubricants Meeting
Toronto, Ontario, Canada
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ABSTRACT

Post-mortem analyses of 50,000 mi (80,000 km) vehicle-aged catalysts revealed that the use of 0.125g Mn/gal (33 mg/L) as MMT (methylcyclopentadienyl manganese tricarbonyl) significantly reduces phosphorus and zinc retention levels at the catalyst inlets by ~20-fold and ~5-fold, respectively. In subsequent laboratory pulsator experiments the presence of 0.016 to 0.157g Mn (as MMT)/gal (4 to 41 mg/L) isooctane fuel containing a 10-fold excess of ZDP (zinc dialkyldithiophosphate, source of oil P and Zn) similarly reduced the retention of P and Zn on TWCs by proportional amounts, while the TWCs maintained significantly higher 3-way conversions than in the absence of MMT. The combustion of Mn from MMT to very stable Mn_3O_4 probably serves as a scavenger in the exhaust for transporting away fuel- and oil-derived catalyst poisons such as P, Zn, and Pb. The utility of the laboratory results will require verification in vehicle studies.

WITH THE SIGNIFICANT REDUCTION in phosphorus (P) levels in fuel, poisoning of automotive catalysts by P is primarily attributed to ZDP (zinc dialkyldithiophosphate) as reported in General Motors studies on underbody pelleted catalysts (1,2,3)* and in Ford studies on low-temperature applications of monolithic catalysts (4,5). The formation of small amounts of amorphous zinc phosphates causes severe deactivation at lower operating temperatures by blanketing the catalyst surface (4). Numerous Japanese patents have attempted to minimize the formation of glassy zinc phosphates by altering catalyst formulations (6) or by adding a getter device in the engine oil recirculating system to reduce levels of ZDP products (7).

Chemical effects of deposits from MMT (methylcyclopentadienyl manganese tricarbonyl), a proposed octane improver, on automotive catalysts have not been found detrimental to catalyst activity. Engine testing of first-generation noble-metal oxidation catalysts (COCs) yielded no evidence of chemical poisoning by MMT (8,9) at levels ≤ 0.125 g Mn/gal (33 mg/L), but physical plugging of catalysts did occur under some conditions. Laboratory simulation of automotive exhaust using pulse-flame combustors burning MMT-containing fuel (0.125g Mn/gal) did not show any chemical poisoning of later generation three-way catalysts (TWCs) beyond that caused by the same fuels without MMT (10).

A cooperative experimental program by the Coordinating Research Council (CRC), involving representatives of the automotive and petroleum industries as well as the EPA and California Air Resources Board (CARB), undertook a comprehensive vehicle testing program (63 cars accumulating over 3 million miles) to determine effects of MMT on emission control systems in 1977-78 California Vehicles (11). The principal conclusion of this study verified that the use of 1/32 and 1/16 g Mn/gal (8.3 and 16.5 mg/L) increased both engine-out and tailpipe HC emissions when compared to clear fuel. However, catalytic converter efficiencies for HC were found 2-3% higher with MMT fuels than with clear fuels after 50,000 mi (80,000 km). Also, MMT did not adversely affect converter efficiencies for CO with COCs or TWCs, or NO_x efficiencies with TWCs (11,12,13).

The present studies provide a possible alternative solution in the event that catalyst deactivation by oil-derived products from ZDP becomes a problem, as in cases when excessive

*Numbers in parentheses designate references at end of paper.

oil consumption combined with lower catalyst temperatures causes catalyst deactivation. The use of Mn (MMT), or perhaps an alkaline earth oxide, could prevent the glassy zinc phosphate formation if it can be introduced in soluble form as a component in the oil additive package or in the fuel. The amount of such a P scavenger would need to be minimized to prevent its excessive accumulation on the catalyst, which could also cause mass transfer limitations or, in an extreme case, severe plugging of catalysts. Accumulation of the scavenger in the combustion chamber in the form of deposits can also increase engine HC emissions.

EXPERIMENTAL

CATALYST FORMULATIONS - Laboratory evaluations were conducted using a commercial Engelhard TWC formulation, M-268D, having a Pt:Rh ratio of 11:1, a precious metal loading of 0.185 wt % Pt + Rh, and proprietary base-metal oxide promoters. Catalysts were prepared on Corning EX-20 monolithic supports having a cell density of 49 square cells/cm² (300 cells/in²) with 300 µm wall thickness. Catalyst buttons 1.9 cm dia. x 1.3 cm long were used in the laboratory studies. Full-sized, race-track shaped cross-section substrates having volumes of 1560 cm³ were employed in the vehicle evaluations.

LABORATORY STUDIES - Catalyst samples were aged on a pulse-flame reactor (14). The technique for pulsator durability and testing of TWCs with air/fuel (A/F) modulation was described previously (15). The pulsator feedgas composition during aging was 0.05% NO, 1.5% CO, 0.2% HC (measured as C₁), and 1.0% O₂ (volume %). During aging the catalysts were cycled at temperatures of 340°, 515°, and 730°C for 17, 77, and 6% of the time, respectively. In the laboratory catalyst aging procedure, the simulated mileages are based on a 30 mph (48 kmph) [or 5000 mi (8040 km)/week] steady-state vehicle operation at a nominal 40,000 h⁻¹ space velocity.

The simulated fuels for pulsator aging utilized isooctane doped with 1.70g ZDP (0.144g P)/gal (449mg ZDP/L) as a source of P. The ZDP doped fuel contained 10-fold higher P input than what is considered a normal oil consumption of 1 quart oil/2000 miles (1L oil/3400 km). MMT was then added at levels of 0.157 and 0.016g Mn/gal (41 and 4 mg/L) to the ZDP-containing isooctane fuel. For the combustion of the non-volatile ZDP, the pulsator combustion was modified with the use of a nebulizer to inject the ZDP-containing isooctane directly into the hot portion of the pulsator furnace for combustion of the fuel. It should be noted that in the vehicle tests described in the next section, MMT was present in the fuel while P and Zn deposits were derived from the ZDP antiwear additive present in the oil. In pulsator experiments,

both MMT and ZDP were additives to the isooctane fuel that was combusted in the pulsator.

Following the pulsator aging, the catalytic steady-state activity was measured at 550°C and 60,000 h⁻¹ space velocity in a separate flow reactor system. A schematic diagram of the apparatus and synthetic gas mixture used was described previously (15). Propylene and propane, representing fast-burning and slow-burning hydrocarbons, respectively, were used in a ratio of C₃H₆/C₃H₈ = 2. The activity and three-way selectivity of the catalysts are reported as a percent conversion of NO, CO and HC as a function of the redox ratio, R, of the reacting gas mixture. (The redox ratio is a ratio of the reducing to oxidizing components in the gas mixture and is determined as follows:

$$R = \frac{\text{CO} + \text{H}_2 + \frac{3n}{n} \text{C}_n\text{H}_{2n} + \frac{(3n+1)}{n} \text{C}_n\text{H}_{2n+2}}{\text{NO} + 2\text{O}_2}$$

Thus, R = 1 corresponds to a stoichiometric gas mixture, while R > 1 represents an overall reducing gas mixture.)

RESULTS AND DISCUSSION

VEHICLE AND ENGINE DYNAMOMETER EVALUATIONS - Post-mortem analyses of TWCs from a Ford fleet revealed that vehicles operated on fuel containing 0.125g Mn (MMT)/gal (33 mg/L) retained substantially less P and Zn contaminants on the catalyst after 50,000 mi (80,000 km) than vehicles operated on fuels without MMT in the fuel. The 14 vehicle fleet was initiated by Ford in 1978 at Southwest Research Institute in San Antonio, TX, for the purpose of testing a synthetic oil as a candidate for an extended oil drain interval (16). The fleet was driven 50,000 mi using an accelerated customer driving schedule (Table 1) which accumulated 1000 mi/week (1600 km) and was representative of 32% highway, 62% suburban, and 6% city driving. Analysis of the fresh oil indicated additive metal concentrations of 1441 ppm P, 1613 ppm Zn, 1871 ppm Ca, and 8 ppm Mg. Oil and fuel consumption results of four 5.0L Granadas fitted only with Engelhard M-268D TWCs are shown in Table 2.

Table 1 - Southwest Research Institute Accelerated Customer Driving Cycle

Traffic	Speed (mph)		Time (min.)	Distance (miles)
	Range	Average		
Suburban	0-45	30.0	105	54
Rest (Engine Off)	0	0	15	0
Suburban	0-45	20.0	20	8
City	0-30	12.0	30	6
Highway	45-60	48.0	40	32
Total		28.6	210	100

Table 2 - Effect of MMT on Contaminant Retention on Catalysts^a from Extended Oil Drain Fleet

5.0L Granada Vehicle	Fuel		Oil Used (ml/qt) ^b	Contaminant wt %		
	(gMn/gal)	(ppm) ^b		P	Zn	Mn
#36	-	16.5	5120	0.92	0.17	0.03
#37	-	16.3	2330	1.40	0.34	0.02
#52	0.125	14.9	1630	0.07	0.07	1.00
#53	0.125	16.1	2080	0.06	0.07	0.00

^aEngelhard TWCs: Pt/Rh = 11 g 40 g/ft³ loading

^b50,000 mi avg.

X-ray fluorescence (XRF) contaminant analysis of the four underbody TWCs from the 5.0L Granadas are also shown in Table 2 after ~50,000 mi. While P retention on TWCs from vehicles #36 and 37 was 0.92 and 1.48 wt % at the inlet, respectively, the retention on TWC inlets from vehicles operated using MMT fuel was only 0.06-0.07 wt % P and ~1% Mn (not sufficient to increase back pressure). This represents ~15-25 fold less P retention in the presence of 0.125g Mn/gal fuel. Similarly, the retention of Zn on vehicles 36 and 37 decreased from 0.17 and 0.34 wt %, respectively, to 0.07 wt % at the catalyst inlet when MMT was present in the fuel. On the inlet face of TWC #52 the retention of lead (Pb) was 0.10 wt %, which was substantially lower than the other 3 catalysts (~0.5 wt %). Since the inlet BET surface area of 2 m²/g was much lower than the others (8-13 m²/g), this TWC may have operated at a substantially higher temperature which could result in lower Pb retention.

The beneficial effects of MMT on reducing the contaminant retention of P, Zn, and Pb on monolithic catalysts is further demonstrated in Table 3 by XRF analyses conducted by Ford Motor Company on vehicle-aged Pt-Pd COCs from three independently operated test programs. These results include COCs from two 351 CID 1975 Ford Torinos (vehicles 1 and 2) which were aged 50,000 mi at Gulf R&D using 91 RON Gulf unleaded gasoline containing <0.005g Pb/gal (1.3 mg/L) and <2 ppm P, with and without 0.125g Mn/gal. Test oil was Gulf SE Quality 10W/40 containing 0.14 wt % P (17). Two 400 CID 1975 Fords (vehicles 3 and 4) were operated by Ethyl Corp. on an EPA-type 50,000 mi durability route (18). Two 351 CID 1976 Mercury Station Wagons (vehicles 5 and 6) operated by Clark Oil Company accumulated 35,000 and 40,000 mi (56,000 and 64,000 km), respectively, using Clark unleaded premium fuel containing ~0.08g Mn/gal (22 mg/L).

Table 3 - Contaminant Analysis of Vehicle-Aged COCs

Ford Vehicle Year-C.I.D.	Fuel MMT gMn/gal	Contaminant wt %				
		Mn	P	Zn	Pb	S
1) 1975-351 ^a	0.125	2.20	0.56	0.04	0.56	0.43
2) "	0	0.14	2.24	0.25	0.93	2.42
3) 1975-400 ^b	0.125	0.97	0.18	x	1.00	0.09 (LHS)
		1.57	0.19	x	0.95	0.10 (RHS)
4) "	0	0.03	1.37	x	3.23	0.06 (LHS)
		0.03	1.57	x	2.93	0.08 (RHS)
5) 1976-351 ^c	0.084	0.61	0.06	0.03	0.63	0.01 (LHS)
		0.65	0.07	0.03	0.55	0.01 (RHS)
6) "	0.084	0.99	0.10	0.06	0.27	0.01 (LHS)
		1.01	0.09	0.06	0.25	0.00 (RHS)

^aGulf R&D aged 50,000 mi

^bEthyl Corp. aged 50,000 mi

^cClark Oil Corp. aged for 5) 35,000 and 6) 40,000 mi

Components in the catalyst formulation were present in similar amounts on the aged catalysts (e.g., ~0.28 wt % Pt, 0.14 wt % Pd, and 1.3% Ce), but contaminant retention of Pb, P, and Zn was markedly less on the COCs aged with fuel containing MMT compared to the unleaded fuels without Mn present. For example, contaminant retention (in wt %) on the COCs from the Gulf test after 50K mi on unleaded fuel averaged 2.24% P + 0.25% Zn + 0.93% Pb, but only 0.56% P + 0.04% Zn + 0.56% Pb when the fuel also contained 0.125g Mn/gal. Also, comparably aged catalysts showing higher Mn deposits retained correspondingly less Pb, e.g., vehicle 5) versus 6).

The average Pb retention of ~3% on catalyst 4) appears excessive (gradient of 5.2 to 1.8% from inlet to outlet) in view of today's average levels of <0.006g Pb/gal in unleaded fuel. However, the maximum allowable Pb levels in unleaded fuel is 0.05g Pb/gal (19). Assuming a consumption of 0.05g Pb/gal for 50,000 mi at 12 mpg, in 1975 for example, would result in ~210 g Pb input to the engine. In this case with 3 wt % Pb retained by 2500g of catalyst (i.e., ~75g Pb total on two catalysts), this corresponds to ~36% Pb retention by the catalyst a typical value. By comparison the 1 wt % Pb retained on catalyst 3) is significantly lowered with the use of MMT and would correspond to only ~12% retention of Pb input by the catalyst.

Table 4 - Effect of MMT on CVS Efficiencies (2.3L Slava Vehicle) and Contaminant Retention of 50,000 mi Vehicle-Aged TWCs^a

Durability veh/clo ^b	Fuel MMT (g/gal)	CVS-CH % Conv. ^c			Contaminant wt % ^d		
		HC	CO	C-NO _x	Pb	P	Mn
2P	0.125	80	65	39	.24	.03	1.10
1P	0	52	31	43	.43	.29	.07

^aEngelhard 80 in³ TWC; Pt/Rh = 11 @ 40g/ft³

^b5000 lb Ford, 400 CID

^cAvg. 3 tests/catalyst on 2.3L slava vehicle with feedback carburetor

^dAvg. of inlet, middle, and outlet sections

Table 5 - Effect of MMT on TWCs^a Pulsator-Aged in the Presence of Excess Oil Phosphorus (ZDP)^b

Fuel MMT g/gal	Contaminant wt %			% Conversion ^c		
	P	Zn	Mn	C-NO _x	CO	HC
a) 0	1.66	0.14	0.10	34	54	41
b) 0.016	0.91	0.10	0.03	66	51	55
c) 0.157	0.06	0.02	0.10	72	76	70

^aEngelhard TWCs: Pt/Rh = 11 @ 40g/ft³ loading

^bCatalyst aging: ~15,000 simulated miles (200h) using isooctane containing 1.7g ZDP (0.144g P)/gal with the indicated Mn concentration

^cActivity measurements: 500°C (932°F); nominal 40,000 h⁻¹ space velocity; pulsator modulation of ± 1 A/V, 0.5 Hz

A correlation of catalyst performance with contaminant retention is shown in Table 4 for TWCs vehicle-aged for 50,000 mi durability in a 1979 Ford fleet test (20). Catalyst durabilities for 50K vehicle mi were completed on 5000 lb vehicles having 400 CID engines with feedback carburetors. Results are shown for 80 in³ TWC volumes pared down from original 95 in³ TWCs in order to directly compare with other emission systems. The CVS-CH efficiencies of the TWCs were then obtained using a 2.3L slava vehicle with a feedback carburetor. Vehicle 2P used fuel containing 0.125g Mn (from MMT)/gal and retained 1.10 wt % Mn after 50,000 mi, but retained only 0.03 wt % P compared to 0.29 wt % P for TWC 1P. TWC 2P also retained less Pb than TWC 1P. The lower contaminant retention levels of Pb and P seem to correlate with better CVS-CH efficiencies.

LABORATORY EVALUATIONS - In subsequent laboratory experiments, a TWC was pulsator durability tested for 15K simulated miles (Table 5) using isooctane containing 0.625g MMT (0.157g Mn)/gal and 1.7g ZDP (0.144g P)/gal (considered ~10-fold higher than normal oil consumption levels). The stabilized conversions of 72% NO, 76% CO, and 78% HC (500°C, R=1.15) indicate substantially improved activity when compared to 34% NO, 54% CO, and 41% HC conversions (Table 5) observed over the same catalyst aged at the same ZDP levels, but without MMT present in the fuel. Steady-state catalyst activities following 15K simulated miles (Fig. 1) also indicate improved catalyst activity during lean conditions and at peak 3-way conversions, and improved NO and CO conversions during rich conditions for the catalyst aged with the MMT-containing fuel. The addition of MMT at 0.016g Mn/gal also improved substantially the NO and HC pulsator conversions with intermediate levels of contaminant retention. Steady-state conversions were nearly identical to that of the 0.157g Mn/gal aging.

The light-off activity (% conversion as a function of temperature) of the aged TWC was improved when aged even in the presence of 0.016g Mn/gal (Fig. 2). The temperature for 80% HC conversion was ~455°C when the TWC was aged with ZDP doped fuel (Fig. 2a), but only ~420°C when the ZDP doped fuel also contained 0.016g Mn/gal. Conversion temperatures for NO and CO were correspondingly lowered by ~50°C for aging with MMT-containing fuel.

XRF analyses indicated 1.66 wt % P and 0.14 wt % Zn retention levels for the catalyst exposed to ZDP doped fuel (Table 5). When 0.157g Mn/gal was added to the ZDP doped fuel, the catalyst retained only 0.06 wt % P (~25-fold less) and 0.02 wt % Zn (~7-fold less) while retaining 0.10 wt % Mn. IR analysis of fuel combustion products indicated the presence of an acidic phosphate identified as ZnH₂P₂O₇ by XRD. Mn products were present but not identifiable.

CONCLUDING REMARKS

The "catalyst enhancement" phenomena (12,21) which resulted in the 2-3% HC improvement in catalyst efficiencies in the CRC study (11) as well as the apparent beneficial effects observed in this study can perhaps be attributed to the scavenging effect of MMT combustion products (22). Manganese in MMT is converted during combustion to Mn₃O₄ (8,10), a very stable end product whose interaction with catalyst components would be minimal. Since Mn was not found chemically associated with P to any significant extent in the combustion products, it is most likely that Mn₃O₄ probably serves as an adsorption site for gaseous contaminants present in the combustion such as Pb halides and Zn phosphates. The fluffy MMT combustion

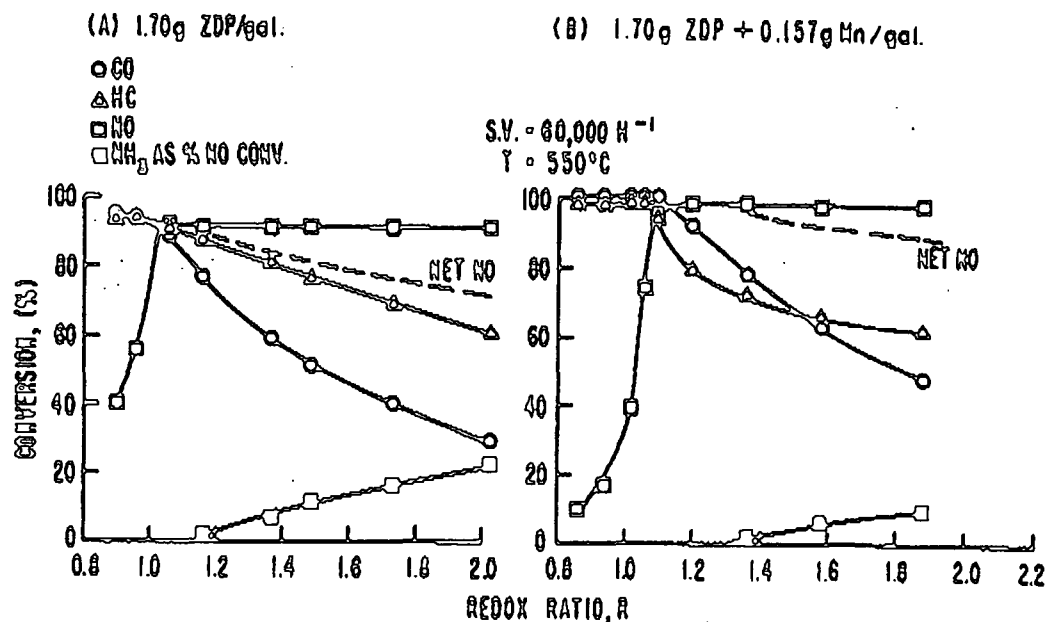


Fig. 1 - Effect of MMT on the steady-state NO, CO, and HC activities of M-268D TWCs pulsator aged 500 h (~15,000 mi) using isooctane containing (A) 1.70g ZDP/gal; (B) 1.70g ZDP + 0.157 g Mn/gal

products have a lower density and higher surface area which would be advantageous for transporting away contaminants such as Pb, P, and Zn. This mechanism would be effective as long as catalyst retention of Mn_3O_4 is not so excessive as to result in mass transfer limitations on the catalyst.

The vehicle data presented using 0.125g Mn/gal indicates retention levels of 1-2% Mn on the catalyst while reducing the levels of P, Zn, and Pb contaminants. Use of 0.125g Mn/gal for 50,000 mi at 12 mpg (1975 estimate) would result in ~520g Mn input. The retention of 2 wt % Mn on a 1100g monolithic catalyst represents 22g or only 4% of the input Mn retained by the catalyst compared to ~35% Pb retention in the absence of MMT. This low retention of Mn is indicative of inert products which are only physically deposited and not chemically bound to the catalyst surface.

The beneficial effects of lower contaminant retention with improved catalyst performance were evident in this laboratory study throughout the range of 0.016 to 0.157g Mn/gal. However, since the use of MMT at the higher levels (e.g., >0.03 Mn/gal) results in increased HC vehicle feedgas levels, adverse engine deposits, and potential catalyst plugging, the optimum Mn levels would be those where the scavenging

for Pb, P and Zn occur with minimal formation and retention of excess Mn_3O_4 deposits. The use of Mn at even the low level of 0.016g Mn/gal as demonstrated in these laboratory studies may lower the retention of contaminants and thereby retain better catalyst performance in vehicle usage. Lower levels of Mn would also decrease the well documented possible effects of Mn_3O_4 deposits which may plug catalysts and oxygen sensors, as well as increase combustion chamber deposits giving rise to higher HC feedgas levels.

The present laboratory data indicate improved catalyst efficiency due to decreased poisoning by P, Pb, and Zn when using MMT even at levels as low as 0.016g Mn/gal. Ultimately, however, the practicality of these opportunities for using Mn as an octane improver, as well as a scavenger of catalyst poisons when necessary, will require verification by vehicle testing.

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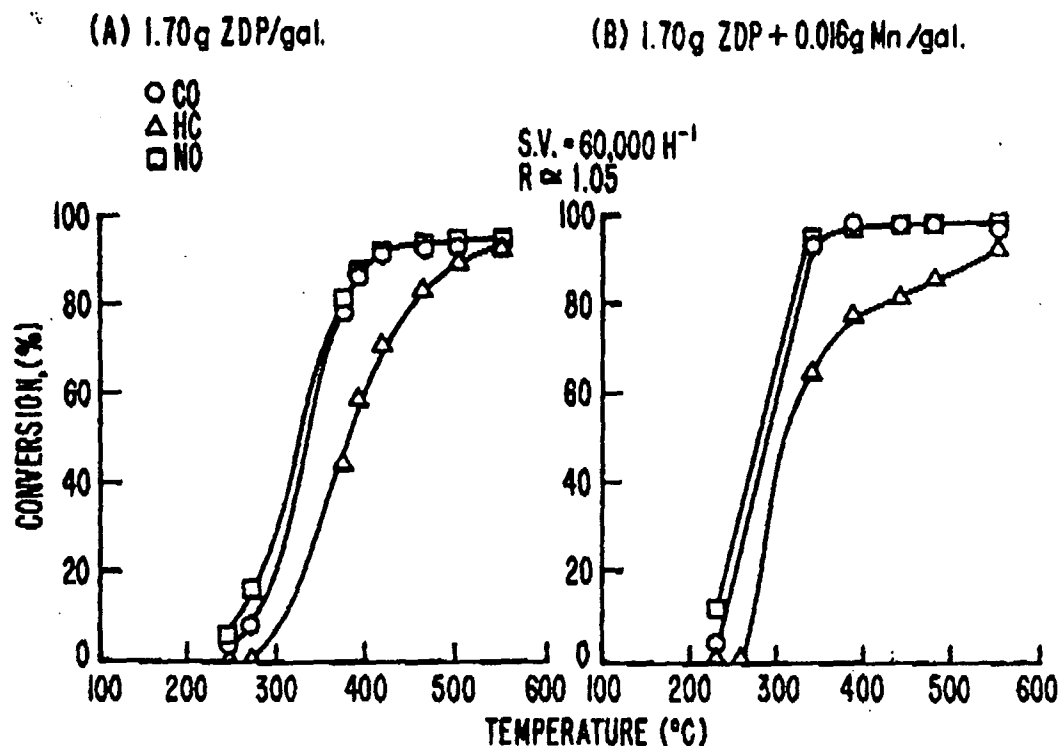


Fig. 2 - Effect of MMT on the light-off activities of M-268D TWCs pulsator aged 500h (~15,000 mi) using iso-octane containing (A) 1.70g ZDP/gal; (B) 1.70g ZDP + 0.016g Mn/gal.

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